Effects of Environmental Factors on 1,3-Dichloropropene Hydrolysis in Water and Soil

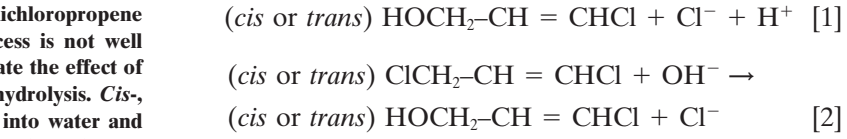
Mingxin Guo,* Sharon K. Papiernik, Wei Zheng, and Scott R. Yates

ABSTRACT

Hydrolysis is the major pathway for fumigant 1,3-dichloropropene (1,3-D) degradation in water and soil, yet the process is not well understood. Experiments were conducted to investigate the effect of various environmental factors on the rate of 1,3-D hydrolysis. *Cis*-, *trans*-1,3-D and their isomeric mixture were spiked into water and Arlington soil (coarse-loamy, mixed, thermic Haplic Durixeralfs) and incubated under different conditions. The rate of 1,3-D hydrolysis in water and soil were evaluated based on its residual amount and Cl^- release, respectively. 1,3-D hydrolyzed rapidly in deionized water, with a half-life of 9.8 d at 20°C. The hydrolysis was pH dependent, with low pH inhibiting and high pH favoring the reaction. Other factors such as isomeric differences, photo irradiation, suspended particles, and small amounts of co-solutes had little effect on the reaction. In soil, 1,3-D hydrolyzed following pseudo first-order kinetics. The hydrolysis rate constant increased with soil moisture content and decreased with the initial 1,3-D concentration. At 20°C, >60% of the 1,3-D applied at <0.61 g kg^{-1} in 10% moisturized soil hydrolyzed within 30 d. The soil particle size and mineralogy had little effect on the reaction rate. Organic matter promoted 1,3-D degradation via direct substitution reactions, and the *trans*-isomer showed preference over the *cis*- to react with certain organic molecules. Microbial contributions were initially insignificant, and became important as soil microorganisms adapted to the fumigant. The results suggest that to accelerate 1,3-D degradation, pH, soil moisture, and organic amendment should be considered.

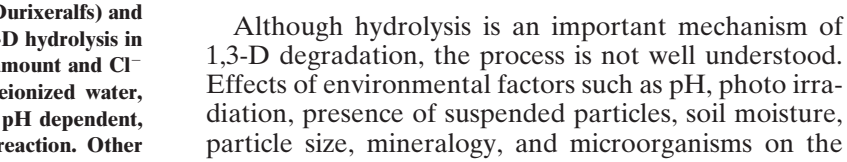
The fumigant 1,3-dichloropropene (1,3-D) is widely used against soil-borne nematodes with an annual consumption of approximately 20 million kg in the USA (USEPA, 2000). Given its acute and chronic toxicity, 1,3-D residue in soil or presence in the aquatic system may cause environmental and health problems. Contamination of groundwater by 1,3-D has been reported in many states in the USA (Parsons and Witt, 1989). To protect groundwater resources, it is essential to swiftly eliminate the chemical from soil after adequate pest-control efficacy has been achieved.

Elimination of 1,3-D in the environment is mainly through biotic and abiotic decomposition processes (Batzer et al., 1996), and hydrolysis is the key mechanism for 1,3-D degradation in water and soil (Castro and Belser, 1966; Roberts and Stoydin, 1976; McCall, 1987). The hydrolysis product is 3-chloroallyl alcohol, which is further transformed to carboxylic acid intermediates (i.e., 3-chloroacrylic acid) and eventually to CO_2. The hydrolysis process can be simply described as:



(*cis* or *trans*) $ClCH_2$–CH = CHCl + H_2O →

(*cis* or *trans*) $HOCH_2$–CH = CHCl + Cl^- + H^+ [1]



(*cis* or *trans*) $ClCH_2$–CH = CHCl + OH^- →

(*cis* or *trans*) $HOCH_2$–CH = CHCl + Cl^- [2]

Although hydrolysis is an important mechanism of 1,3-D degradation, the process is not well understood. Effects of environmental factors such as pH, photo irradiation, presence of suspended particles, soil moisture, particle size, mineralogy, and microorganisms on the hydrolysis reaction need to be investigated. In sterile aqueous solutions, the hydrolysis of 1,3-D is significant, and the reported half-life is approximately 11 d at 20°C (McCall, 1987). Predicted from its structure, 1,3-D hydrolysis should be a mixture of unimolecular (S_N1) and bimolecular (S_N2) nucleophilic substitution reactions, in which water molecule or hydroxide ion serves as the nucleophile (Schwarzenbach et al., 1993). Accordingly, the concentration of OH^- is expected to be important in the reaction, especially at high pH values (i.e., pH ≥ 10). van Dijk (1974) reported a higher hydrolysis rate of 1,3-D in pH 7.5 buffer solutions than in pH 5.5 buffer solution at both 15 and 29°C. Nevertheless, McCall (1987) observed an independence of the 1,3-D hydrolysis rate on the solution pH over a range of 5 to 9. To better understand the hydrolysis process, the effect of pH should be clarified.

Suspended particles and dissolved organic matter (DOM) are common components in natural water systems and may affect 1,3-D hydrolysis. Sunlight and microorganisms may also promote the reaction. So far, few studies have been conducted to investigate these aspects. Castro and Belser (1966) examined 1,3-D hydrolysis in phosphate buffer solutions and soil slurries (soil/water = 3:1 to 1:2), and found that hydrolysis rates (evaluated by the Cl^- release) were significantly higher in the soil slurries than in water. It is unclear whether the rate enhancement in the presence of soil was due to soil microorganisms or to reaction with soil components.

In soil, 1,3-D is mainly degraded through biotic and abiotic hydrolysis (Castro and Belser, 1966; Roberts and Stoydin, 1976; Verhagen et al., 1995). The reported half-life of 1,3-D in soil ranges from 1.8 to 61 d at 25°C (van Dijk, 1980; Batzer et al., 1996). It is uncertain what factors control the hydrolysis rate. Considering that 1,3-D may react directly with OM (Gan et al., 1998) and be entrapped in soil matrix as persistent residues (Guo et al., 2003), its hydrolysis rate in soil is generally overestimated if evaluated by the disappearance. Since the hydrolysis process of organic halides is generally irreversible (Schwarzenbach et al., 1993), in sterile soils

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Abbreviations: 1,3-D, 1,3-dichloropropene; DOM, dissolved organic matter; IC, ion chromatography; OC, organic carbon; UV, ultraviolet.

with low OM contents, the hydrolysis rate of 1,3-D may be determined by the Cl^- release.

To control its residue in soil and persistence in water, hydrolysis of 1,3-D warrants systematic studies. The objectives of this study were to evaluate the effect of environmental factors such as pH, suspended particles, cosolutes, photo irradiation, soil particle size, moisture, organic matter, mineralogy, and microorganisms on 1,3-D hydrolysis and to determine half-lives of 1,3-D in water and soil.

MATERIALS AND METHODS

Chemicals and Soil Materials

1,3-D isomeric mixture (49% *trans* + 49% *cis*) and *cis*-1,3-D (97% purity) were obtained from Chem Service (West Chester, PA). *Trans*-1,3-D (analytical standard) was provided by Dow Agrosciences Co. (Indianapolis, IN).

Arlington sandy loam soil (coarse-loamy, mixed, thermic Haplic Durixeralfs) was collected from the Ap horizon (0–18 cm) of the University of California Agricultural Experiment Station in Riverside, CA. The soil was typical of that used in California fumigated agriculture, and the section from which the soil was collected was never treated with 1,3-D or other fumigants. The soil has an organic carbon (OC) content of 9.2 g kg^{-1}, clay content of 74 g kg^{-1}, and pH 7.20. It was air-dried, sieved to <2 mm, and stored at 20°C before use. A Florida muck soil (pH 7.16, OC 460 g kg^{-1}) sampled from the Everglades Research and Education Center (Belle Glade, FL) was also used as an organic amendment.

Hydrolysis in Water

To test 1,3-D hydrolysis in water, 8.00 mL of deionized water was pipetted into 8.5-mL headspace vials (clear borosilicate glass). The vials were capped with aluminum seals and Teflon-faced butyl rubber septa, autoclaved at 121°C for 60 min, and spiked with 40 μL of ethyl acetate solution containing 105 m*M* *cis*-, *trans*-, or isomeric mixed 1,3-D, using a 100-μL gas-tight syringe. The final concentration of 1,3-D in solution was 58.6 mg L^{-1}. For better sealing effects, the vial heads were further dipped into melted paraffin wax to cover with a thin layer of the material. The vials were wrapped with Al foil to exclude light, and incubated at 20 ± 1°C with constant shaking. At predetermined times, triplicate vials were removed, 0.5 mL of the solution was taken from each vial with a 0.5-mL gas-tight syringe, and extracted with 5 mL ethyl acetate and 3.0 g anhydrous Na_2SO_4. The extracts were analyzed by GC for *cis*- and *trans*-1,3-D contents.

To investigate the effect of photo irradiation on 1,3-D hydrolysis in water, vials spiked with *cis*-, *trans*-, or isomeric mixed 1,3-D, with and without Al foil wraps, were placed under fluorescent light of 3 W m^{-2} in the laboratory at 23°C and under direct sunlight (550–720 W m^{-2} at 1200 h) outdoors without temperature control (9–32°C). At scheduled times, triplicate vials were taken out, and solutions were extracted and analyzed for remaining 1,3-D.

To determine the effect of pH, 0.05 *M* H_2SO_4, pH 4.00 buffer (0.1 *M* formic acid–sodium formate), pH 7.00 buffer (0.1 *M* NaH_2PO_4–Na_2HPO_4), pH 10.00 buffer (0.1 *M* $NaHCO_3$–Na_2CO_3), and 0.1 *M* NaOH solutions were used instead of deionized water to carry out the experiment following the procedures described above.

To examine effects of clay and organic particle suspensions, 40 mg of Na^+-montmorillonite (treated to <2 μ*M*, Clay Minerals Repository, Univ. of Missouri, Columbia, MO) or oven-dried Florida muck (sieved to <75 μ*M*) was added into 8.00 mL deionized water, autoclaved, and incubated with 1,3-D as described above.

To investigate inorganic salt and DOM effects, Arlington soil–water extracts (pH 7.20, EC 4.13 dS m^{-1}, Cl^- 1.24 m*M*, SO_4^{2-} 1.13 m*M*, $H_2PO_4^-$–HPO_4^{2-} 24.11 m*M*, DOC 47.8 mg L^{-1}) and Florida muck–water extracts (pH 7.16, EC 1.09 dS m^{-1}, Cl^- 0.52 m*M*, NO_3^- 0.02 m*M*, SO_4^{2-} 1.82 m*M*, $H_2PO_4^-$–HPO_4^{2-} 4.63 m*M*, DOC 848.2 mg L^{-1}) were used in place of deionized water in the hydrolysis experiment. Nonsterilized water extracts of Arlington soil and Florida muck were also employed to investigate the microbial effect.

Hydrolysis in Soil

Hydrolysis of 1,3-D in soil was examined on the basis of Cl^- release from fumigated sterile Arlington sandy loam. Briefly, air-dried soil was adjusted to 10% gravitational moisture content, and aliquots of 11-g moist soil were weighed into 25-mL serum bottles, capped with aluminum seals and Teflon-faced butyl rubber septa, and autoclaved at 121°C for 60 min. *Cis*-, *trans*-, or isomeric mixed 1,3-D (82 μL) was injected into the sterilized soil with a 100-μL gas tight syringe. The 1,3-D application rate was 10 g kg^{-1} soil. The bottles were further sealed with a thin layer of paraffin wax on heads, and set in the dark at 20°C. At scheduled times, triplicates were taken out and soils were spread on Al foil in a fume hood and evaporated for 24 h to dissipate remaining 1,3-D. The soils were then put back into their original bottles, and 10.00 mL of 0.01 *M* $NaNO_3$ water solution was added to extract Cl^- for 1 h under shaking. Following extraction, the slurries were centrifuged at 10 900 × *g* for 15 min, and supernatants were analyzed for Cl^- concentrations by ion chromatography (IC). Soils without 1,3-D spiking were treated as controls and were handled using exactly the same procedures. Amounts of Cl^- resulting from the chemical application were used to index 1,3-D hydrolysis.

To investigate the effect of soil moisture on 1,3-D hydrolysis, air-dried Arlington soil was adjusted to gravimetric moisture contents of 5, 10, and 15% with deionized water, and incubated with 1,3-D as described above.

Air-dried Arlington soil was further ground to completely pass through a 0.25- or 0.075-mm sieve, and the three particle-sized soils (<2, <0.25, and <0.075 mm) were adjusted to 10% moisture content and treated as described above to examine the effect of soil particle size on 1,3-D hydrolysis. The chemical composition of the three particle-sized soils was the same.

To investigate the effect of soil OM, Arlington soil was amended to OC 30.7 g kg^{-1} with oven-dried Florida muck, adjusted to 10% moisture content, sterilized, and incubated with 1,3-D. The hydrolysis experiment was also conducted with nonsterilized Arlington soils to examine the microbial effect. The effect of soil mineralogy was tested by conducting the hydrolysis experiment with Na^+-montmorillonite (Univ. of Missouri Source Clay Minerals Repository, Columbia, MO), Na^+–kaolinite (Ward's Natural Science Establishment, Macon, GA), hematite (Fisher Scientific, Fair Lawn, NJ), and quartz sand (<0.075 mm) at 20% water content.

Chemical Analysis

Cis- and *trans*-1,3-D in ethyl acetate extracts were analyzed with a HP5890 GC system (Hewlett-Packard, Avondale, PA) with an electron capture detector and an DB-VRX fused silica capillary column (30 m long by 0.25 mm i.d. by 1.4 μm film thickness). The carrier gas (He) flow rate, inlet temperature, oven temperature, and detector temperature were set as

1.2 mL min^{-1}, 230°C, 120°C, and 280°C, respectively. The analysis time for each sample was 15 min, and the injection volume was 2.0 μL without split. The method detection level for *cis*- or *trans*-1,3-D isomer in water was 40 μg L^{-1}.

Chloride ion in soil water extracts were analyzed by an IC DX-100 system (Dionex Corp., Sunnyvale, CA) consisting of an IonPac AS14 ion exchange column, two AG14 guard columns, a conductivity detector, and an AS40 automated sampler. A mobile phase comprising 7.5 m*M* Na_2CO_3 and 2.5 m*M* $NaHCO_3$ was employed, the flow rate was 1.2 mL min^{-1} and the run time was 13 min per sample. The method detection level for Cl^- in soil was 3 μmol kg^{-1}.

RESULTS AND DISCUSSION

Hydrolysis of 1,3-D in Water

In deionized water, 1,3-D degraded at a relatively high rate following pseudo first-order reaction kinetics (Fig. 1). At 20°C, *cis*- and *trans*-1,3-D (spiked separately and as a mixture) had an identical half-life of 9.8 d. With GC-MS techniques, *cis*- and *trans*-3-chloroallyl alcohols were identified in the incubated solutions, and Cl^- was detected by IC. Accompanying the production of chloroallyl alcohols and Cl^-, a dramatic pH decrease due to the release of H^+ in the solutions was observed. For example, when deionized water was spiked with 58.6 mg L^{-1} (0.53 m*M*) of 1,3-D, the pH decreased from 7.00 to 3.80 in 4 d, and to 3.21 in 20 d. It is evident that 1,3-D hydrolyzes in deionized water following the reaction described in Eq. [1] and [2].

The Effect of pH

As illustrated in Fig. 2, 1,3-D hydrolyzed more rapidly in alkaline solutions than in acidic solutions, demonstrating the significance of the solution pH. Hydrolysis of 1,3-D is a mixed S_N1/S_N2 reaction, with water or OH^- as nucleophiles (Schwarzenbach et al., 1993). In the S_N1 reaction, the hydrolysis rate is independent of the concentration of nucleophiles, and the process follows first-order kinetics. In the S_N2 reaction, the hydrolysis rate is a function of concentrations of both 1,3-D and nucleophiles (H_2O and OH^-). Since OH^- exhibits a much higher nucleophilicity (4.2) than water molecule (0, Schwarzenbach et al., 1993), it competes strongly with the latter in the hydrolysis reaction, and the effect becomes more significant as the solution pH increases. The contribution of OH^- in the S_N2 reaction was demonstrated by the large increase in hydrolysis rate as the buffer pH increased from 7 to 10 (Fig. 2). In the acidic range, the effect of pH was weak yet did exist, reflected by a slightly but significantly ($P < 0.003$ by paired *t* test) higher hydrolysis rate in the pH 4 buffer solution than in 0.05 *M* H_2SO_4 (Fig. 2). Likely, the increase of solution acidity decreased the activity of water molecule (formation of H_3O^+) and the concentration of OH^-, thus inhibiting the S_N2 hydrolysis. Due to the confounding effects, it was impractical to sort out the separate contributions of S_N1, H_2O in S_N2, and OH^- in S_N2 in the hydrolysis reaction. Given the relatively constant concentration of OH^- in the solutions in the experiments, the hydrolysis of 1,3-D in all solutions could be described using a first-order kinetic model (Fig. 2). At 20°C, half-lives of 1,3-D in 0.05 *M* H_2SO_4; pH 4.0, 7.0, and 10.0 buffer; and 0.1 *M* NaOH solutions were 10.5, 8.7, 7.2, 2.8, and 2.3 d, respectively. Although McCall (1987) reported that the rate of 1,3-D hydrolysis in aqueous buffer solutions was independent of pH over a range of 5 to 9, our data covering a larger range in pH demonstrate that 1,3-D hydrolyzes at high pH more rapidly than at low pH. O'Connor (unpublished report, 1990) also observed some slight pH dependence of the hydrolysis rate of *cis*-1,3-D at 25°C in pH 4, 7, and 9 buffer solutions. It is noteworthy that hydrolysis of 1,3-D in deionized water is slower than in pH 4 or 7 buffer solutions. This is because deionized water has no buffering capacity, H^+ resulting from 1,3-D hydrolysis (Eq. [1]) makes the water a strongly acidic solution (e.g., pH of deionized water decreased to <4 within 4 d after spiking 1,3-D at 60 mg L^{-1}), decreasing the activity of H_2O and concentration of OH^-.

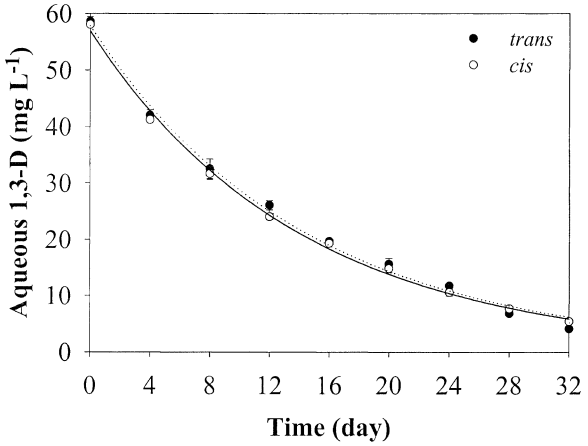

Fig. 1. Hydrolysis of 1,3-D (separate isomers) in deionized water. Symbols represent the mean of triplicate samples and error bars indicate the standard deviation. Dotted and solid lines are first-order fitted curves for *trans*- and *cis*-isomers, respectively.

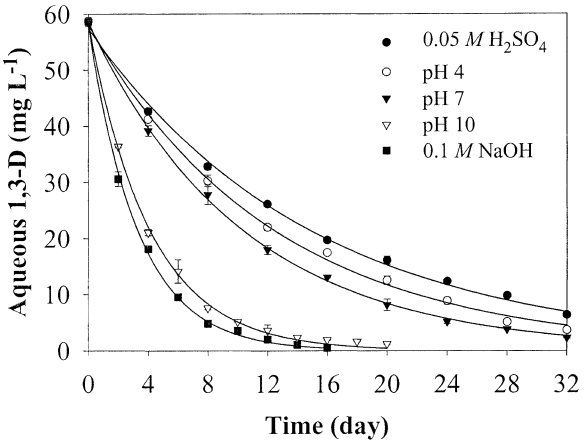

Fig. 2. The effect of pH on 1,3-D hydrolysis. Data presented are *trans*-isomers. Symbols represent the mean of triplicate samples and error bars indicate the standard deviation. Lines are first-order fitted curves.

The Effect of Photo Irradiation

After 32 d of direct exposure under sunlight and fluorescent light, little effect of photo irradiation on 1,3-D

Table 1. First-order hydrolysis rate constants k (d^{-1}) and half lives $t_{1/2}$ (d) of 1,3-D in aqueous solutions and under different conditions (number of observations = 27).

Treatments	Autoclave	Irradiation	Isomer	$k \pm$ SE (r^2)	$t_{1/2}$
Water	sterile	dark	*cis-*	0.070 ± 0.0023 (0.995)	9.8
	sterile	dark	*trans-*	0.071 ± 0.0019 (0.997)	9.7
	sterile	sunlight	*cis-*	0.069 ± 0.0027 (0.993)	10.1
	sterile	Sunlight	*trans-*	0.071 ± 0.0021 (0.996)	9.7
Soil extract	sterile	dark	*cis-*	0.071 ± 0.0046 (0.983)	9.7
	nonsterile	dark	*cis-*	0.072 ± 0.0027 (0.994)	9.6
Muck extract	sterile	dark	*cis-*	0.071 ± 0.0030 (0.992)	9.7
	nonsterile	dark	*cis-*	0.074 ± 0.0033 (0.992)	9.4
Clay suspension	sterile	dark	*trans-*	0.073 ± 0.0023 (0.996)	9.5
Muck suspension	sterile	dark	*trans-*	0.076 ± 0.0031 (0.993)	9.2

hydrolysis were observed. Hydrolysis rates were not statistically different between *cis-* and *trans*-1,3-D isomeres in the dark and under photo irradiation ($P > 0.6$, Table 1), suggesting that light had no significant effect on the rate of 1,3-D hydrolysis. Although the vials (borosilicate glass) used in the experiment may partially absorb ultraviolet (UV) radiation (Koller, 1965), it is presumed that UV radiation has little direct influence on 1,3-D hydrolysis based on photolysis reactions in the air. In air, decomposition of 1,3-D is mainly by reaction with free radicals and ozone (Tuazon et al., 1984). Vapor phase photolysis of 1,3-D is insignificant, and direct photo-transformation occurs only in the presence of atmospheric particles (Li, 1979). Thus, photo irradiation (light) may not be an important consideration in handling 1,3-D if temperature is controlled.

The Effect of Inorganic Salts and DOM

Hydrolysis of 1,3-D in Arlington soil water extracts (pH 7.20) and Florida muck water extracts (pH 7.16) occurred at similar rates as in the deionized water ($P > 0.15$, Table 1), demonstrating that 1,3-D hydrolysis in aqueous solutions was not significantly influenced by the presence of a small amount of soluble inorganic salts or DOM. Although the water extracts contained inorganic anions such as NO_3^-, SO_4^{2-}, and HPO_4^{2-} and organic anions (DOC 848.2 mg L^{-1}) that had higher nucleophilicities than water molecule (Schwarzenbach et al., 1993), enhanced hydrolysis or transformation of 1,3-D was not observed. Considering the much higher concentrations of inorganic salts and DOC in these soil and muck extracts compared to in natural waters, it is inferred that in natural aquatic systems, the effect of co-solutes on 1,3-D hydrolysis may not be significant.

The Effect of Suspended Particles

Hydrolysis of 1,3-D in the montmorillonite suspension followed a similar rate as in deionized water ($P > 0.53$, Table 1), demonstrating no significant effect of added clay particles. Evidently, clay mineral surface-catalyzed 1,3-D hydrolysis, if any, was insignificant. The hydrolysis experiment was further conducted with 1:1 Arlington soil water slurries, and a similar hydrolysis rate as in water was observed.

In water with Florida muck addition at 5 g L^{-1}, concentrations of residual 1,3-D were slightly yet consistently lower than in deionized water in a range of 0.4 to 2.5 mg L^{-1} through the experiment period. However, the degradation rate constant was not significantly different from that in deionized water (Table 1), suggesting little catalytic effect of organic particles on 1,3-D hydrolysis. The low concentrations may be a result of rapid reactions of 1,3-D with the added organic matter or sorption on the solids.

The Effect of Microorganisms

Hydrolysis of 1,3-D occurred at similar rates in sterilized and nonsterilized Arlington soil water extracts or Florida muck water extracts ($P > 0.50$, Table 1), demonstrating that microorganisms in the extracts did not promote 1,3-D degradation. It was suspected that microbial activities might be inhibited due to the high initial concentration of applied 1,3-D (59 mg L^{-1}) or lack of O_2 in the vials, so the hydrolysis experiment was reconducted with 10 mg L^{-1} 1,3-D in 5-mL extracts (headspace 3.5 mL), and similar results were obtained. Microbial species capable of rapidly decomposing 1,3-D have been reported in soils regularly treated with the fumigant (Verhagen et al., 1995). Such microbes may not abundantly exist in the soil and muck used in these experiments, which were never treated with 1,3-D. Deionized water may not be able to extract microbes that can use 1,3-D as substrate from the Arlington soil or Florida muck, or the extracted microorganisms may not have adapted to the presence of 1,3-D in the time required for these experiments. In waste water contaminated by 1,3-D, bacteria that use the chemical as carbon and energy sources may abound after a certain time period of adaptation. Katsivela et al. (1995) isolated five species of 1,3-D-degrading bacteria on biofilms after long adaptation phases of the community in mineral salt water containing 1 m*M* 1,3-D. However, these bacteria were fairly susceptible to environmental changes, and could not be enriched using standard batch-enrichment techniques. In our experiments, hydrolysis of 1,3-D was mainly an abiotic process.

Hydrolysis of 1,3-D in Soil

Hydrolysis of 1,3-D in soil was determined from Cl^- release. When 1,3-D was spiked at 10 g kg^{-1} (90 mmol kg^{-1}) into sterile Arlington soil (10% moisture content, 20°C), 8.5 mmol kg^{-1} of Cl^- was generated in 30 d, which accounted for 9.5% of the potential Cl^- production assuming a complete initial hydrolysis (removal of one Cl atom from each 1,3-D molecule). It is postulated that at such a high spiking rate, most of the 1,3-D re-

mained in the headspace, and only the portion that diffused into the water layer on soil particle surfaces underwent hydrolysis. The static sealed vials used in these experiments provided poor gas-exchange conditions, and the diffusion of spiked 1,3-D into soil water was highly dependent on the initial concentration. Consequently, the absolute amount of 1,3-D that experienced hydrolysis (based on Cl^- production) increased with the initial concentration, yet the relative percentage decreased. When we reduced the application rate to 0.61 g kg^{-1}, approximately 62% of the applied 1,3-D hydrolyzed in 30 d, and the resulted Cl^- production in soil was 3.4 mmol kg^{-1}, equivalent to 40% of that at an application rate of 10 g kg^{-1}. Although the cumulative Cl^- release followed first-order kinetics (Fig. 3), it is inappropriate herein to estimate the hydrolysis rate constant or half-life of 1,3-D in soil because of the initial-concentration dependence. Ma et al. (2001) also found that the 1,3-D disappearance rate was highly dependent on the initial concentration, with first-order rate constants varying 1.5- to 4-fold for the concentration range of 0.6 to 60 mg kg^{-1}. It is expected that a large proportion of spiked 1,3-D will hydrolyze in soil (10% moisture) in 30 d at a typical field application rate of 0.16 g kg^{-1}.

The Effect of Moisture

Moisture plays an important role in 1,3-D hydrolysis. Tests with Arlington sandy loam at 5, 10, and 15% moisture show that the Cl^- release from 1,3-D hydrolysis was remarkably greater under higher soil moisture conditions ($P < 0.01$, Fig. 3). The effect of soil moisture content may be ascribed to two aspects. On the one hand, dissolution of 1,3-D in water was limited at low moisture contents, and the hydrolysis reaction was hindered. On the other hand, sorption of 1,3-D onto soil matrix was inhibited at high moisture contents, which in turn, promoted the hydrolysis reaction. In soils from four different locations, van Dijk (1980) observed significantly higher dissipation rates of 1,3-D at the moisture content of field holding capacity than at plant withering points. Gan et al. (1999) reported that degradation of 1,3-D in a Carsitas loamy sand (mixed, hyperthermic Typic Torrpsamments) increased linearly with soil moisture content over a range of 2 to 16%. The more rapid hydrolysis of 1,3-D at higher moisture contents suggests that water sealing after 1,3-D application is an effective method via physical blocking and chemical degradation to decrease fumigant atmospheric emission from the field.

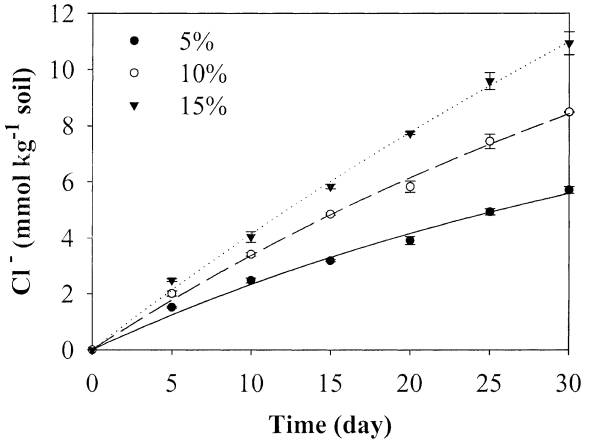

Fig. 3. Chloride release from hydrolysis of 1,3-D (10 g kg^{-1}) in soils with different moisture contents. Symbols represent the mean of triplicate samples and error bars indicate the standard deviation. Dotted, dashed, and solid lines are fitted curves for 5, 10, and 15% moisture content, respectively.

The Effect of Soil Particle Size

Arlington soils ground to <2, <0.25, and <0.075 mm were incubated individually with 1,3-D. At 10% moisture content, Cl^- releases from the three soils were similar ($P > 0.1$), suggesting that particle size had little effect on 1,3-D hydrolysis. It is inferred that clay minerals do not contain catalytic sites for 1,3-D hydrolysis reactions, and soil particle size is unimportant in the process. In closed systems, van Dijk (1980) observed that 1,3-D disappeared much more rapidly in clay soils than in sandy soils, but this effect may have been due to the higher pH of the former (pH 7.3) than the latter (pH 4.6).

The Effect of Soil Mineralogy

When 1,3-D was incubated at 10 g kg^{-1} with montorillonite, kaolinite, hematite clay, and fine quartz sand (20% moisture), the rate of Cl^- release was similar ($P > 0.1$, Fig. 4), suggesting that soil mineralogical effects on 1,3-D hydrolysis may be insignificant. The hydrolysis reaction may occur on the surface of soil particles, but these clay minerals apparently do not function as catalysts, and the specific surface area is not important. This contention is strengthened by the fact that in water–clay suspensions and 1:1 soil slurries, 1,3-D dissipated at similar rates as in deionized water. Combined with the insignificant effect of soil particle size, it may be deduced that soil texture does not affect 1,3-D hydrolysis.

The Effect of Organic Matter (OM)

In Arlington soil amended with 5% Florida muck, the release of Cl^- resulting from 1,3-D degradation was

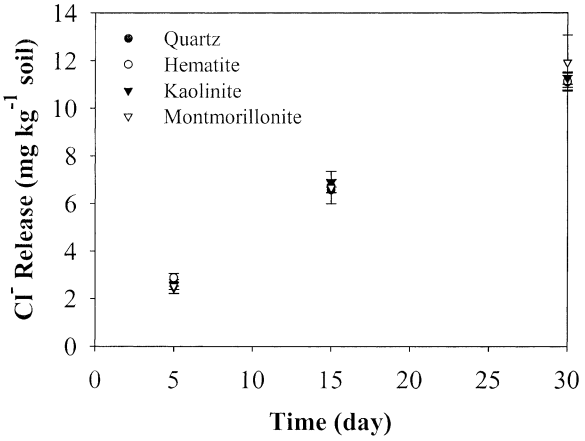

Fig. 4. Chloride release from hydrolysis of 1,3-D (10 g kg^{-1}) in different mineralogical matrixes. Symbols represent the mean of triplicate samples and error bars indicate the standard deviation.

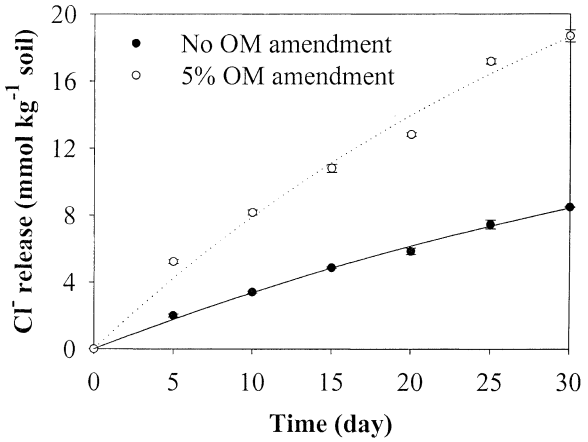

Fig. 5. Chloride release from hydrolysis of 1,3-D (10 g kg^{-1}) in unamended and organic matter amended soils. Symbols represent the mean of triplicate samples and error bars indicate the standard deviation. Dotted and solid lines are fitted curves for unamended and 5% Florida muck amended Arlington soils, respectively.

remarkably accelerated ($P < 0.001$, Fig. 5). The acceleration may be a result of promoted hydrolysis, or substitution of OM functional groups with C(3)-Cl in 1,3-D molecules. Considering that OM addition (5 g L^{-1}) yielded a slightly lower (0.4–2.5 mg L^{-1}) concentration of remaining 1,3-D in water yet had little effect on the overall hydrolysis rate (Table 1), we rather believe the latter. Soil OM contains nucleophilic groups such as $–NH_2$, –SH, –OH, –COOH that may participate in the substitution. Rapid substitutions of $–NH_2$ in aniline for Cl in 1,3-D to produce 3-chloroallyl aniline have been observed by Gan et al. (1998). For further confirmation, 1,3-D was spiked at 10 g kg^{-1} into 10% moisturized Arlington soils with and without 5% Florida muck amendment in sealed 21-mL headspace vials, and incubated for 20 d. The remaining 1,3-D in OM amended soils was drastically lower, while 3-chloroallyl alcohol, a major hydrolysis product, was only slightly higher than in the unamended soils (Fig. 6). Organic matter may

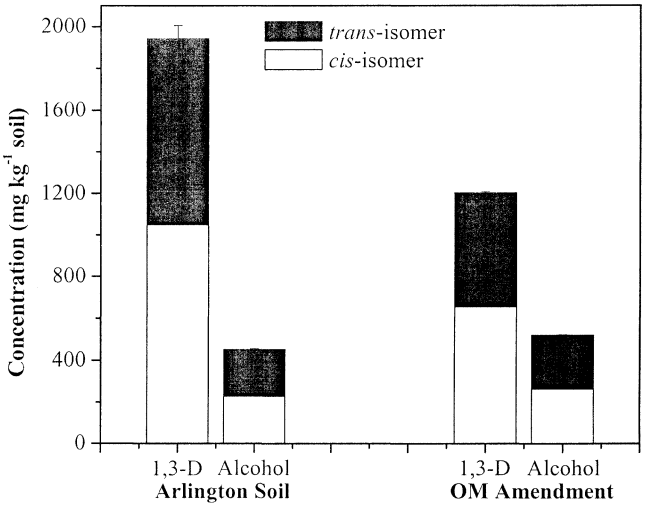

Fig. 6. Remaining 1,3-D (10 g kg^{-1} spiking rate) and generated chloroallyl alcohol in unamended and OM amended soils. Symbols represent the mean of triplicate samples and error bars indicate the standard deviation.

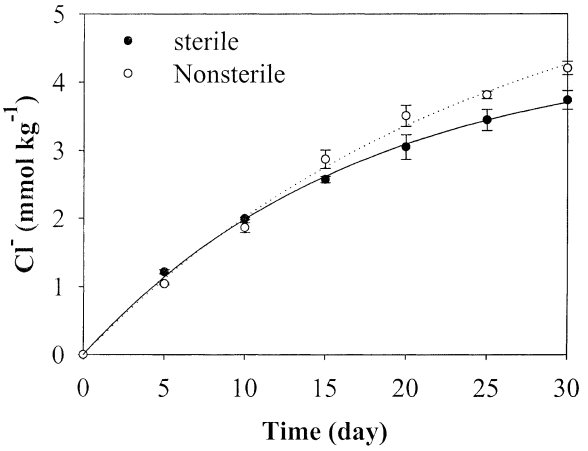

Fig. 7. Microbiological hydrolysis of 1,3-D (1.0 g kg^{-1}) in soil. Symbols represent the mean of triplicate samples and error bars indicate the standard deviation.

not react directly with 3-chloroallyl alcohol; otherwise the concentration of 3-chloroallyl alcohol would be lower in the OM amended soil. Therefore, it may be concluded that soil OM promotes 1,3-D degradation, but not via hydrolysis.

The Effect of Soil Microorganisms

In nonsterile and sterile Arlington soils, Cl^- release from 10 g kg^{-1} of 1,3-D application were nearly identical. Because microbial activities may be inhibited at such a high fumigation rate, the incubation experiments were repeated with 1.0 g kg^{-1} of 1,3-D spiking. In sterile soils, initially the release of Cl^- was slightly higher than in nonsterile soil, probably due to the autoclave effect that helped activate soil OM. Cumulatively released Cl^- increased more rapidly in nonsterile soils, after 10 d of incubation time, Cl^- production in nosterile soils exceeded that in autoclaved soils, and the difference became greater as the incubation progressed ($P < 0.003$, Fig. 7), indicating significant microbial contributions in 1,3-D hydrolysis. In a 14-d incubation experiment, Verhagen et al. (1995) found that microbial degradation of 1,3-D was minor in three mineral soils without a history of fumigation. After six repeated fumigations, 1,3-D spiked in these adapted soils was degraded rapidly.

The Isomeric Effect

In sterilized Arlington soil, initially *trans*-1,3-D generated Cl^- much more rapidly than *cis*-isomer, and both isomers had identical Cl^- release rates after 5 d (Fig. 8). Tests with 0.61 g kg^{-1} 1,3-D in nonsterile and sterile Arlington soil with or without 5% Florida muck amendment showed similar scenarios. The initially higher rate might be a result of direct reaction of *trans*-1,3-D with certain soil components, such as organic constituents. Likely, certain organic molecules may react rapidly with *trans*- but not *cis*- isomers owing to the steric difference. As the particular organic compounds were depleted, release of Cl^- from the two isomers became similar. This was corroborated by the lower remaining concentration of *trans*- than *cis*-isomers in unamended and

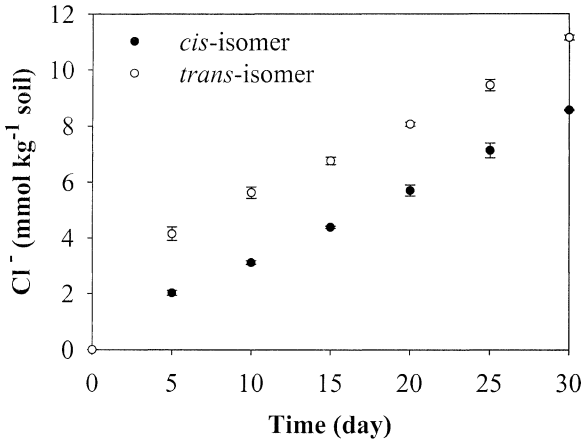

Fig. 8. Isomeric effects on hydrolysis of 1,3-D (1.0 g kg^{-1}) in soil. Symbols represent the mean of triplicate samples and error bars indicate the standard deviation.

OM-amended Arlington soils after 20 d of incubation with initially identical spiking of the two isomers (Fig. 6). Gan et al. (1998) also observed that *trans*-1,3-D was degraded more rapidly than *cis*-isomers in nonsterilized and sterilized, compost amended Arlington soils (judged by the chemical disappearance rate). The equivalent Cl^- release rates of *cis*- and *trans*-isomers after 5 d suggested that the isomeric effect on 1,3-D hydrolysis in soil is insignificant.

CONCLUSIONS

Fumigant 1,3-D was not stable in water, and it hydrolyzed to 3-chloroallyl alcohol and Cl^- at a relatively high rate. The half-life of 1,3-D in deionized water at 20°C was 9.8 d. Solution pH influenced 1,3-D hydrolysis significantly, with low pH inhibiting and high pH favoring the reaction. Half-lives of 1,3-D in pH 4, 7, and 10 buffer solutions were 8.7, 7.2, and 2.8 d, respectively. Factors such as photo irradiation, suspended particles, small amounts of soluble inorganic salts and DOM had little effect on the reaction. In unadapted solutions, microbial contributions to 1,3-D hydrolysis were insignificant, and *cis*- and *trans*-isomers hydrolyzed at identical rates. Hydrolysis of 1,3-D in water is primarily a chemical process that is mainly controlled by temperature and pH.

In soil, hydrolysis of 1,3-D is comparatively slow, and is concentration dependent. At an application rate of <0.60 g kg^{-1}, >60% of the applied 1,3-D was hydrolyzed within 30 d in 10% moisturized Arlington soil at 20°C, judged by the Cl^- release. Soil particle size and mineralogy had little effect on 1,3-D hydrolysis, while moisture content influenced the process significantly. 1,3-D hydrolysed more rapidly as soil moisture increased in a range of 5 to 15%. Organic matter promoted 1,3-D degradation via direct substitution reactions, but did not affect the hydrolysis reaction. *Trans*- and *cis*-1,3-D hydrolyzed in soil at equivalent rates, and the former showed preference over the latter to react directly with particular organic molecules in soil. Microbial accelerated hydrolysis was initially insignificant, and became important as soil microorganisms adapted to the fumigant.

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